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(58) Field of search

H1B

(54) Leakage detection

(57) The invention relates to a method for the detection of leakages from electrochemical cells having a nonaqueous electrolyte and alkali metal or alkaline earth metal anodes. Materials leaking from such cells form acids when coming into contact with the atmosphere, and these are detected by applying to the surface of such cells a coating containing an acid base indicator in a suitable carrier, preferably an adhesive.

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SPECIFICATION **Leakage Detection**

This invention relates to indicators for detecting leakage of acids, generated by leakage of precursor materials from cells and batteries, and from sealed electrolyte containers used in said cells and batteries.

Electrochemical cells in which alkali and alkaline earth metals act as the anode, containing nonaqueous electrolytes which in addition may serve as the cathodic depolarizer, are becoming increasingly important for cells and batteries developed for industrial, military and consumer markets. The cells offer a high energy density, wide operating temperature range and a long operating and shelf life (up to 10 years). The long operating and shelf life make it necessary to manufacture hermetically sealed cells, usually using a glass-to-metal seal to insulate between the positive and negative terminals, and hermetic welding of the cover to the case by suitable means such as laser, plasma or tungsten inert gas (TIG) welding. Loss of electrolyte from the cells and batteries may decrease the operating life of the cells, may form corrosive materials such as sulfur dioxide, chlorine and hydrogen chloride upon contact with atmospheric moisture, and in some type of cells may produce hazardous conditions.

Indicators have been previously used with certain electrochemical systems and especially in systems with an aqueous electrolyte, to warn for leakage of electrolyte from the sealed cell. U.S. patent 4,222,745 described a method for leakage detection of sulfur dioxide from cells, employing potassium dichromate absorbed on finely divided silica and mixed with polymeric adhesive material.

The object of this invention is to provide simple means and a simple method for the detection of electrolyte leakage from cells or batteries, where the leaking component upon reaction with atmospheric moisture decomposes to produce acidic compounds.

The present invention relates to a composition comprising a mixture of (1) an acid-base indicator or a mixture of indicators dissolved in (2) a suitable adhesive material. Acid-base indicators change their color in the presence of acid. The color change may take place either in the visible wavelength region or in the ultra-violet wavelength region. A partial list of acid-base indicators and the pH at which the color change takes place can be found in "Text Book of Quantitative Inorganic Analysis", A. I. Vogel, Longmans, England—Third Edition—1961, Page 51.

The adhesive material usually consists of an organic binder, pigments (sometimes omitted), and a carrier liquid (sometimes omitted). The binder is a high molecular weight polymer which may or may not be cross-linked. The pigments, which may be organic or inorganic, contribute primarily to opacity, color, adhesion and particularly to rheological properties of the coating in the fluid form. After application of a smooth coating, the carrier liquids are removed usually by heating or vaporation; polymerization is then initiated by heat, by

atmospheric oxygen, by water vapor or exposure to an electron beam or to ultraviolet radiation, depending on the binder.

The adhesive materials are preferably cured at room temperature upon exposure to atmospheric moisture, or they may be heat cured. These adhesive materials may be originally transparent, translucent or containing colored pigments, so as to form a color contrast between the indicator color and the object on which they are spread. The adhesive may be in the form of a paste, glue lacquer, cement or resin of natural or synthetic origin. Adhesives of natural origin include for example lacquers such as shellac (animal extraction), and resins such as gum arabic of vegetable extraction. Synthetic adhesives are represented by thermoplastic lacquers (air-dried thermoplastic) such as vinyl chloride vinyl acetate copolymer, acrylates, chlorinated rubber, polyamides, vinyl or vinylidene chloride-acrylonitrile copolymers, vinylacetate nylons, cellulosic esters, polyesters and others. Synthetic adhesives may be represented by thermosetting materials such as epoxies, polyamides and others, and silicones. A partial list of synthetic resins used for coating may be found in the book titled "Encyclopedia of Chemical Technology", by Kirk-Othmer, Third edition, Volume 6, PP.428 and 459—462.

The adhesive material may be used to protect a corrosion sensitive area, such as a weld, by forming a surface resistant film.

In preparing the composition of this invention the indicator may be dissolved in an organic solvent, of that quantity which is just sufficient to effect dissolution of the indicator. In addition, the organic solvent should dissolve in the polymeric adhesive without affecting its properties. The mixture of indicator and the organic solvent is added, while stirring to the polymeric adhesive. The stirring period can vary from 0.5—10 hours to accomplish homogeneous mixing depending on the viscosity of the polymeric adhesive. The amount of indicator generally ranges from about 0.1 to 400 parts by weight of indicator per 10,000 parts by weight of polymeric adhesive material.

Preferred solvents are acetone, methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof. Convenient acid base indicators are Methyl red, Methyl orange, Bromocresol green, Alizarin, Eosin, Bromocresol purple, Fluorescein, Thymol blue and Cresol red.

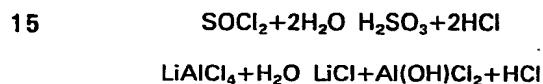
As the adhesive a one-component, side-stripping lacquer, based on a polyamide resin, an acrylic resin or a vinyl chloride—acetate resin or a two-component lacquer based on a Biphenol/Epichlorohydrin resin or on a phenolic resin are preferred, eg. 4—40 parts of Methyl red indicator dissolved in 10,000 parts of one-component lacquer based on polyamide resin.

The adhesive may be a polydimethyl or other silicon rubber.

In a preferred arrangement the cell contains thionyl chloride, sulfur dioxide, sulfonyl chloride, phosphoryl chloride, or mixtures thereof, a non-

aqueous solution of LiAlCl_4 or AlCl_3 , or their mixtures, chlorine, bromine monochloride, bromine, nitrous oxide, sulfur trioxide or sulfur dioxide dissolved in a non-aqueous organic or inorganic solvent, a solution of LiBr in a mixture of sulfur dioxide and acetonitrile.

Some of the materials in the cell are precursors for more than one acid. For instance, a solution of lithium aluminum chloride (LiAlCl_4) in thionyl chloride, which serves as the electrolyte in commercial lithium cells and batteries, yields upon contact with atmospheric moisture hydrogen chloride (HCl) and sulfurous acid (H_2SO_3) according to the equations



Because of the nature of the indicator mixture, it can be applied to the casing of cells and batteries, and to glass and metallic electrolyte containers in reserve cells and batteries, which may be subject to leakage of precursors which generate acids on contact with atmospheric moisture.

The following examples describe particular uses of an indicator, its color change and the electrochemical systems used. These are given as examples only and are not intended to limit the scope of this invention.

EXAMPLE 1:

Methyl Red Indicator Powder (0.50 gr.) was dissolved in 10 ml. of acetone. This solution was added to 1000 gr of one component, thermoplastic side stripping lacquer based on polyamide resin.

The resulting slurry was stirred for 2 hours. The resulting mixture is yellow in color. A thin film was spread on a metallic surface and allowed to dry. In the presence of thionyl chloride vapor the yellow film changed to red.

EXAMPLE 2:

A mixture according to Example 1 was spread on the cover of a lithium cell containing electrolyte 1.2M LiAlCl_4 in thionyl chloride. The cell leaked through the glass-to-metal seal. The color of the indicator turned to red.

EXAMPLE 3:

A metallic surface as in Example 1 was sprayed with a white adhesive such as RTV 112. After drying overnight, it was sprayed with an additional thin layer of methyl red as in Example 1. The color of the indicator layer changed to red upon exposure to thionyl chloride. The white background made the color change more pronounced.

EXAMPLE 4:

The mixture of Example 1 was spread on a heat sealed area of glass ampoule which contained an electrolyte of 1.2M LiAlCl_4 in thionyl chloride. This ampoule is part of a reserve cell. A leakage in the sealing caused a color change of the indicator from yellow to red.

EXAMPLE 5—9:

Runs were conducted in which 2.5 gr of each of the 5 indicators listed in Table 1, dissolved in a 19 ml of acetone. This solution was added to 1000 gr of a resin composition defined in Example No. 1.

Each of the resulting slurries was stirred for 2 hours. A thin film of each of the resulting slurries was spread on a metallic surface, allowed to dry, and then was exposed to thionyl chloride vapor.

Table 1 summarizes for each indicator the color change taking place in the presence of thionyl chloride vapor.

TABLE 1

Example Number	Indicator	Color Change
5	Methyl orange	Yellow to orange
6	Bromocresol green	Blue to colorless
7	Alizarin	Pink to colorless
8	Eosin	Red to yellow
9	Bromocresol purple	Blue to colorless

EXAMPLES 10—15:

The mixture according to examples 1 and 5 to 9 were spread on metallic surfaces, and were exposed to sulfur chloride vapors. Color changes took place similar to those obtained in Examples 1 and 5 to 9 (as summarized in Table 1), respectively.

Examples 16 to 21:

The mixtures according to examples 1 and 5 to 9 were spread on metallic surfaces, and were exposed to sulfur dioxide (SO_2). Color changes took place similar to those obtained in Examples 1 and 5 to 9 (as summarized in Table 1), respectively.

EXAMPLES 22—27:

The mixtures according to examples 1 and 5 to 9 were spread on the case of commercial Li/SO_2 cells. The electrolyte in these cells is LiBr and acetonitrile, dissolved in liquid sulfur dioxide. An intentional leakage brought about by piercing a small hole in the cell case made the indicators to change their color similarly to the changes in Examples 1 and 5 to 9 (as summarized in Table 1), respectively.

EXAMPLE 28:

A quantity of 1.5 gr of cresol red indicator was dissolved in 10 ml of acetone. This solution was added to 1000 gr of a one-component acrylic lacquer. The resultant slurry was stirred for 0.5 hours. A thin film of the resulting slurry was spread on a metallic surface, allowed to dry at room temperature and then exposed to thionyl chloride vapor. The color of the film color changed from yellow to violet.

EXAMPLE 29:

A mixture similar to that of Example 28 was

prepared, but using Methyl Orange as the indicator. Upon exposure to thionyl chloride vapors, the film color changed from yellow to red.

EXAMPLES 30—34:

- 5 Runs were conducted in which 1.5 gr of each of the 4 indicators listed in Table 2, were dissolved in 10 ml of MEK (Methyl Ethyl Ketone). This solution was added to 1000 gr of the hardener component of a two-component lacquer. The resin is based on
- 10 Biphenol-Epichlorohydrin. The two components of the epoxy lacquer were mixed in the appropriate ratios just before it was used. The slurry was spread on a metallic surface allowed to dry at room temperature, and exposed to thionyl chloride vapor.
- 15 Table 2 summarizes for each film the color change in the presence of thionyl chloride vapor.

TABLE 2

Example No.	Indicator	Color Change
30	Alizarin (no-salt)	Violet to red
31	Cresol Red	Yellow to violet
32	Thymol Blue	Yellow to red
34	Methyl Red	Orange to red

EXAMPLE 35:

- 20 A quantity of 1.0 gr of Methyl Red indicator was dissolved in 5 ml of Methyl Iso-butyl Ketone (MIBK). This solution was added to 750 gr of a one-component lacquer based on vinyl chloride and vinyl-acetate. The resultant mixture was stirred for 1
- 25 hour. A thin film of the resulting mixture was spread on a metallic surface, allowed to dry at room temperature and exposed to thionyl chloride vapor. The color of the film changed from red to violet.

EXAMPLE 36:

- 30 A mixture similar to that of Example 35 was prepared, using methyl orange as the indicator. Upon exposure to thionyl chloride vapors the film color changed from orange to brown.

EXAMPLE 37:

- 35 A composition was prepared comprising a polyamide resin as in Example 1, with 0.2 g methyl red and 100 g fine titanium dioxide per 1000 g of adhesive. The change from yellowish to clear pink was clearly distinguishable when a leakage
- 40 occurred.

- The foregoing Examples are given as illustrative of the advantages of the present invention and it is understood that changes and variations can be made without departing from the scope of the present invention as defined in the following claims.
- 45

CLAIMS

1. A method of detecting a leakage from nonaqueous electrolyte cells or batteries with alkali and alkaline earth metal anodes, where the leakage

50 materials from cells, batteries or electrolyte containers in reserve cells or batteries form acids upon contact with atmospheric moisture, which comprises applying to surfaces of cells or batteries a coating of an acid-base indicator in an adhesive.

55 2. The method according to claim 1 in which the composition contains 0.1 to 400 parts by weight of an acid-base indicator per 10,000 parts by weight of adhesive.

3. A method according to claim 2, where the acid-base indicator is first dissolved in an organic solvent and which is dissolved in the adhesive material.

4. A method according to claim 3, wherein the organic solvent is acetone, methyl ethyl ketone, methyl isobutyl ketone, or a mixture thereof.

5. A method according to claim 1, wherein the acid-base indicator is selected from Methyl red, Methyl orange, Bromocresol green, Alizarin, Eosin, Bromocresol purple, Fluorosein, Thymol blue and

70 Cresol red.

6. A method according to claim 1 wherein the adhesive material is a one-component, side-stripping lacquer, based on a polyamide resin, an acrylic resin or a vinyl chloride-acetate resin.

75 7. A method according to claim 1 wherein the adhesive material is a two-component lacquer based on a Biphenol/Epichlorohydrin resin or on a phenolic resin.

8. A method according to claim 7, wherein 4—40 parts of Methyl red indicator is dissolved in 10,000 parts of one-component lacquer based on polyamide resin.

9. A method according to claim 1 wherein the adhesive material is a silicone rubber.

85 10. A method according to claim 9 wherein the silicone rubber is a polydimethylsiloxane.

11. A method of claim 1 wherein the cell contains thionyl chloride, sulfur dioxide, sulfuryl chloride, phosphoryl chloride, or mixtures thereof, a non-aqueous solution of LiAlCl_4 or AlCl_3 , or their mixtures, chlorine, bromine monochlorine, bromine, nitrous oxide, sulfur trioxide or sulfur dioxide dissolved in a non-aqueous organic or inorganic solvent, a solution of LiBr in a mixture of

95 sulfur dioxide and acetonitrile.

12. An electrochemical cell having a non-aqueous electrolyte containing a substance which when coming into contact with humidity in the atmosphere forms an acid, characterized in that to the surface of the cell or to part thereof, there is applied a substance changing its color in a suitable adhesive matrix.

13. An electrochemical cell according to claim 12, wherein the substance undergoing the color change is an acid/base indicator.

105 14. An electrochemical cell according to claim 12, or 13 wherein the adhesive matrix is a polymeric substance compatible with the substance undergoing the color change.

110 15. An electrochemical cell according to any of claims 12 to 14, wherein a matrix is a thermoplastic resin.

16. An electrochemical cell according to any of claims 12 to 15, wherein the substance undergoes a

col r change visibl in the UV region.

17. An electr chemical cell provided with a surface coating on at least part of its surfac ,

substantially as hereinbefore described and with
5 refer nce to any of the Examples.

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